**Eigenfunctions/values of**

So going back to:



We ascertained that the eigenfunctions/values were, in principle. But we were particularly interested in writing down simultaneous eigenfunctions of the operators L2, S2, J2, Jz in terms of the simultaneous eigenfunctions of L2, S2, Lz, Sz. And also interested in knowing what j, mj eigenvalues were consistent with having an L2 quantum number ℓ, and S2 quantum number s. We’ll set about answering this question via a ‘differential’ approach to solving the eigenvalue equation. Our differential equation will be more like a difference equation rather, but the spirit of this approach is similar to the one with which we’ve written down eigenvalue equations in the past.

**‘Differential equation’ approach to solving for eigenvectors/values of coupled representation**

First, let’s recognize that these eigenfunctions must be linear combinations of the eigenfunctions of L2 and S2 – else they wouldn’t satisfy the L2 and S2 eigenvalue equations. So the eigenfunctions can be written as:



Now then let’s first start out by determining the eigenfunctions of the Jz operator. The eigenfunctions would obey the equation:



For this equation to be true, we see that whatever mj is, cmℓ,ms must be 0 if mℓ + ms ≠ mj. So the sum over mℓ and ms is restricted to only those values for which mℓ + ms = mj. Further, the range of values that mj could take on are limited to those that could come out of the range of mℓ + ms. The largest this could be is ℓ + s, and the smallest it could be is

-ℓ - s. Additionally, mℓ and ms decrement/increment by values of 1, so mj must also. So we see that:



The coefficients cmℓ,ms are called the Clebsch-Gordon coefficients by the way. There are tables which list the various values for a given j and mj, but we will attempt to determine them ourselves, by looking at the J2 equation next. So let’s fill this into the J2 equation.



Projecting this equation onto the orbital/spin momentum basis (the uncoupled basis in other words) we have:



So we have the eigenvalue/vector equation to solve, switching the ′ and un′ indices for prettiness.



Maybe progress can be made by filling in the **L** and **S** vectors, and then evaluating the action of Sz and Lz at least.



We can evaluate the matrix elements by writing Lx, Ly and Sx, Sy in terms of the L and S raising and lowering operators…



Let’s recall the action of creation/annihilation operators on an L, S eigenket.



and similarly for S. Before we work this out, let’s observe that the only terms which will survive the sum are the L+S-, L-S+ terms. This is because the sum is over those terms which have the same value of mℓ′ + ms′, and to keep the sum the same we would have to raise and lower mℓ′ and ms′ by opposite amounts. So this simplifies our expression to (factoring out the 1/4):



The δ functions collapse the sums, and leaves us with,



This is the equation for the Clebsch-Gordon coefficients, and implicitly the eigenvalues j and mj too. The equations are a little too difficult to solve in generality I think, so let’s take a special case.

**Solution of the Clebsch Gordon recursion relation for ℓ = 1, s = ½.**

The simplest non-trivial case we could get away with is where ℓ = 1, and s = ½. Let’s write down the equation for each coefficient, keeping in mind that there cannot be any coefficients with mℓ or ms indices not equal to -1,0,1, or – ½ , ½ respectively. We’ll go case by case for each possible mℓms value for that cmℓ,ms guy on the right hand side.

***Case: mℓ = 1, ms = ½.***

Then we have:



The only way for this equation to be true, besides having c1,1/2 = 0 (which would not be desirable) for the [ ] to be 0, which entails…



which in our case works out to j = 1 + ½ = 3/2. Additionally mj = mℓ + ms = 3/2. And the ket which corresponds to these values is the c1,1/2 ket, i.e.,

|ℓ=1, mℓ=1> |s=1/2,ms=1/2>. So we have one eigenfunction:



(remember what all the numbers mean?) This is interesting since it says that when the particle is in its maximum Lz and Sz state, then it is also in its maximum Jz and J2 state. Before we were saying that if we know Lz and Sz, then we couldn’t know J2 because the J2 operator doesn’t commute with Lz and Sz. And this is true in general, but we see that it is not true for *every* single state.

***Case: mℓ = 1, ms = -1/2***

Then we have:



Filling in the creation/annihilation operator coefficients we have:



and so we have:



We’ll leave this alone for now and go on to the next,

***Case: mℓ = 0, ms = 1/2***

Then we have:



Filling in the creation/annihilation operator coefficients we have:



Filling these in we have:



Next,

***Case: mℓ = 0, ms = -1/2.***

Then we have:



Evaluating the creation/annihilation operator coefficients…



Filling these in we get:



Next,

***Case: mℓ = -1, ms = ½***

Then we have:



Filling in the operator coefficients…



Filling these in…



And lastly,

***Case: mℓ = -1, ms = -1/2***

We have:



Again, in order for the coefficient not to be zero, we must have the bracket to be zero. Then we have:



once again. So j = 3/2, and of course mj = mℓ + ms = -3/2. So this is the case where the orbital and spin angular momenta are ‘aligned’ in negative z direction. And we see that this eigenket associated with this is just the one with the c-1,-1/2 coefficient, i.e., |ℓ=1,mℓ = -1>|s=1/2,ms=-1/2>. So we have:



***Putting leftover equations into matrix form and solving***

So out of our six equations, we were able to immediately solve two, but had four left over. One thing we have learned, and is generally true, is that when the orbital and spin angular momenta are both in the highest or lowest values, then the total angular momentum quantum number is at its maximum jmax = ℓ+s, and z-component total angular momentum quantum number is at its max/min mj = jmax/-j­max respectively. So in other words,



So we’ve determined, as it turns out, the maximum value that j may take on. But we haven’t determined what other values j may take on. To do that we need to examine our other four equations, reproduced here:



There are 4 undetermined coefficients and four equations. Let’s put these in matrix form,



In order for the coefficients to have non-zero solutions, the matrix must be singular, so setting the determinant to zero we get (this is a block diagonal matrix so the determinant is just the product of the block diagonal determinants)



The roots for x are: 3/4 and 15/4. Solving for j then we get 3/2 and 1/2. So these are the allowed values of j. What are the eigenvectors associated with these? Let’s examine the 3/2 first. Plugging in j = 3/2 we get:



Multiplying the first row by 1/√2 and adding to the second, and multiplying the third row by 1/√2 and adding the second we get:



c1,-1/2 can be anything – we’ll say A. Then c0,1/2 must be √2A. c0,-1/2 can be anything – we’ll say B, and then c-1,1/2 must be B/√2. So we have:



So there are two more eigenvectors associated with j = 3/2. The first has mj = ½ (obtained by adding up mℓ and ms) and so we have:



upon normalization. The second has mj = -1/2 and so we have:



upon normalization. So we see that mj can take values of 3/2, ½, -1/2, and -3/2, consistent with that fact that mj = -j, -j+1, …, j. Now let’s look to the last value, j = ½. Plugging that into our matrix we get:



Adding appropriate linear combinations we get:



So we see that c1,-1/2 = A, which implies in the equation above that c0,1/2 = -A/√2. Then third up implies c0,-1/2 = B, and then the top implies that consequently c-1,1/2 = -B√2. So the eigenvectors are:



So there are two eigenvectors associated with j = 1/2. The first has mj = ½ (obtained by adding up mℓ and ms) and so we have:



upon normalization. The second has mj = -1/2 and so we have:



upon normalization. So we see that mj can take values of -1/2, and ½, consistent with that fact that mj = -j, -j+1, …, j.

**Summary of ℓ = 1, s = ½ results**

Summarizing then, our results are that for the case ℓ = 1, s = ½, j can take on two values, namely j = ℓ + s = 3/2, and j = ℓ-s = ½. And in either case, mj = -j, -j +1, …, j. And in terms of the uncoupled basis, the eigenvectors are:



We can put this in the position/spin basis by projecting the eigenvectors against <**r**|<ms| to get:



So we get our first taste of wavefunctions that have a mixing between spin and spatial components. This might seem weird at first, but it is no different than a wavefunction mixing x and y coordinates. Of course *that* might seem weird to someone who only lives in 1 dimension.

**General rules distilled from our example above**

Of course we only solved the differential equation for ℓ = 1, s = ½, the simplest case. What about higher cases. What are the allowed j and mj eigenvalues then? We noticed above that the highest j was jmax = ℓ+s, and that the lowest j was jmin = |ℓ-s|. And further that mj varied between –j and j in unit steps. We can argue generally that this must be the case. Namely that for a given ℓ and s, the allowed values of j run in integer steps between jmin = |ℓ-s|, and jmax = ℓ+s. And that the allowed values of mj run between –j and j.



We can prove this by noting the uncoupled representation of the angular momentum of a particle has a total of (2ℓ+1)(2s+1) basis states, for a given ℓ and s. And so the coupled representation must have the same number of basis states. And we can prove that this prescription on the allowed values of j and mj does match this number of states. For the total number of states would be (assume ℓ > s for the sake of discussion):



So there you go. The only other thing we need to complete the analysis, is some way of knowing what the Clebsch-Gordon coefficients, cmℓ,ms are. As we saw, obtaining them from the ‘differential equation’ above is rather laborious. Luckily there are tables that one can use to look them up for a given j and mj. Nonetheless, there is one more technique that one can use to obtain them with much less effort than above (though not less effort than the table) and it is usually the preferred method.

**Appendix: Result for ℓ arbitrary, s = 1/2**

Well reviewing what we did, and observing that our matrix was block diagonal, it occurs to me that we *can* actually solve the equations in general, without too much work, for ℓ arbitrary and s = ½. This would involve diagonalizing a 2×2 matrix. In general we can solve for s arbitrary, but would have to diagonalize a (2s+1)×(2s+1) matrix. So we want,



So for given ℓ and s, j can be either ℓ - s or ℓ + s. mj can range between -j and j of course. And note since ms = ±s = ±1/2, for a given mj, mℓ can take on two values at most, namely mj – s, or mj + s. So we can say,



where again, s = ½. Then let’s go back to our Clebsch-Gordon recursion equation:



where I’ll recall,



and examine the equation for these two coefficients,



and cross out the two terms there because we cannot have any coefficients with spin indices greater than ½ or less than -1/2. And also recognize that the same colored coefficients are the same. We can now write, simplifying some of those subscripts, and the [ ] thing:



and then, using s = ½ intermittently,



And so,



Let’s see what those C terms are:



So they’re the same. Now our equations are:



In matrix form, looks like:



For a non-zero solution to these equations, these rows must be linearly dependent, and must be so for any of our allowed values of j and mj. Or in other words, the determinant of our matrix must be zero. Let’s check,



where we’ve used s = ½ again. Let’s fill in j = ℓ±s, and we’ll liberally use s = ½.



So this checks out. That’s nice. So take note of this identity, the consequence of the bottom line in that block of equations just above the set immediately above:



So going back to our matrix and eliminating the bottom row of our matrix equation, say, via row operations, the solution to our matrix equation is:



where k can be anything. Let’s use our purple identity to simplify this a little bit:



where k´ is just another constant, and we recognize that ℓ(ℓ+1) + s2 = (ℓ+s)2 since s = ½. This better improve fast. Well we should normalize it so we need:



which brings us to:



So can write this as:



This reproduces our earlier results sans an occasional overall factor of -1, but overall phase factors don’t matter. And we’ll remember the ± signs are for j = ℓ ± s, in that order.

**Example**

Consider the electron in the 3𝑑1 orbital of a lone scandium atom. A weak magnetic field is applied in the 𝑧 direction such that the perturbing Hamiltonian is given by: 𝛿𝐻 =𝜇𝐵(𝛼𝐿𝑧+𝛽𝑆𝑧) (α and β are real constants). Assume that when the 𝐽z and 𝐽2 operators are applied to the electron's state, the results are 3ℏ/2 and 35ℏ2/4 respectively. Calculate the first-order correction to the electron's energy due to the perturbing Hamiltonian without using the projection theorem (based on the Wigner-Eckart theorem).

So we know that the electron has quantum numbers s=1/2, ℓ = 2, j = ?, and mj = 3/2. Since j(j+1) = 35/4, we must have j = 5/2 (trial and error, or do quadratic formula). Then we just need to break this |ℓsjmj> state down into |ℓsmℓms> states. Well we can use our formula above:



Filling in our numbers,



j = ℓ + s, so we use the top sign,



Now we’ll use first order perturbation theory (see those files),

